**USEPA REGION 9 LABORATORY**
**RICHMOND, CALIFORNIA**

# STANDARD OPERATING PROCEDURE 530
# ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

Revision 9
Effective Date: June 14, 2013

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This SOP was prepared by ICF International for the United States Environmental Protection Agency under the Region 9 Environmental Services Assistance Team (ESAT) contract (USEPA contract no. EP-W-06-041). ESAT Document Control Number: 01305020-15971

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## 1 SCOPE AND APPLICABILITY

This method is applicable for drinking, ground, surface, and saline water, domestic and industrial wastes, and solids leached with reagent water. This method applies to the determination of the inorganic anions fluoride, chloride, nitrite, bromide, nitrate, orthophosphate, and sulfate by ion chromatography for use in the USEPA Region 9 Laboratory, Richmond, California. This SOP is based on EPA Method 300.0, *Determination of Inorganic Anions by Ion Chromatography*, Revision 2.1, August 1993. Deviations from the reference method are described in Appendix A. Analytes and quantitation limits (QLs) for this analysis are listed in Appendix B.

## 2 METHOD SUMMARY

A small volume of sample is injected onto a series of ion-exchange columns. The anions of interest separate on the basis of their relative affinities to a low capacity, strongly basic anion exchanger. The separated anions are directed into a strongly acidic cation suppressor exchanger where they are converted to their highly conductive acid forms. The carbonate and bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are detected by electrical conductivity and are qualitatively determined on the basis of retention time as compared to the standards. Quantitation is based on peak areas. A quadratic calibration is used to determine concentrations in environmental samples for fluoride, nitrite, bromide, nitrate, chloride, orthophosphate, and sulfate.

## 3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the EPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

There are no analysis-specific definitions in this SOP.

## 4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the EPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

### 4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample

handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Safety precautions must be taken when handling solutions and samples. Protective clothing including lab coats, safety glasses, and gloves must always be worn. If solutions come into contact with your eyes, flush with water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. ESAT personnel should contact the Group Leader or Health and Safety and Environmental Compliance Task Manager and EPA staff should see the Team Leader or the Laboratory Safety, Health and Environmental Compliance Manager (LaSHEM) to determine if additional treatment is required.

4.2 Equipment and Instrument Hazards

Areas of high, lethal voltages exist within the instrument. Never touch parts of the instrument that are not intended for access by the instrument operator. Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *EPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact

of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP.

### 4.4 Waste Management

The EPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with EPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure* and City of Richmond Discharge Permit. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA Laboratory Safety, Health, and Environmental Manager or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

| Waste Stream Description | Waste Label | Hazard Properties |
|---|---|---|
| Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.) | Non-hazardous Waste | Not applicable |
| Anions analysis waste (aqueous carbonate, bicarbonate solution) | Hazardous Waste | Not applicable |

## 5 SAMPLE HANDLING AND PRESERVATION

### 5.1 Containers and Required Sample Volume

Samples should be collected in pre-cleaned plastic or glass bottles. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis, and minimize waste disposal. A 100 mL sample volume of water or 20 g of solid sample should be sufficient to meet these objectives.

### 5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Anions samples may initially be received in either Room 207 or Room 503. Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Sample Storage

Samples should be received and stored at > 0 °C to ≤ 6 °C. If not already noted in the LIMS login record, record any discrepancies in the LIMS memo field.

Retain samples for 60 days after the final analytical report is sent to the data user.

5.4 Holding Time

The maximum sample holding time for nitrite-N, nitrate-N, and *ortho*-phosphate-P is 48 hours from the time of sample collection. For fluoride, chloride, bromide, and sulfate, the holding time is 28 days from the date of sample collection.

## 6 INTERFERENCES

1. Interferences can be caused by substances with retention times that are similar to an overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification with concentrated eluent can be used to solve most interference problems associated with retention times. See Section 8.3.4.4 for procedures employed to prevent reporting false negative results for nitrite in the presence of chloride.

2. The water dip or negative peak elutes near and can interfere with the fluoride peak. This effect does not typically occur under conditions described in this SOP. When other measures fail, this interference can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (100x) to 100 mL of each standard and sample. See Section 8.3.3 for measures to address interference from the water dip.

3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4. Samples and reagents that contain particulates require filtration to prevent damage to instrument columns and flow systems.

5. Large concentration of acetate anion, which elutes early during the chromatographic run, affects retention times of target analytes. This method is therefore not recommended for acetic acid leachates.

## 7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

### 7.1 Instruments and Equipment

- Ion Chromatograph - The Dionex Ion Chromatograph System including Advance Chromatography Module, Pump, Conductivity Cell Detector, Dionex Advance Computer Interface, Dionex AS40 Autosampler, and Dionex PeakNet 6/Chromeleon 6 Data System or equivalent that meets the requirements of the method.
- Anion Guard Column, AG14-4mm from Dionex or equivalent
- Anion Separator Column, AS14-4mm from Dionex or equivalent
- Anion Self-Regenerating Suppressor ASRS, Ultra 4mm from Dionex or equivalent
- Analytical Balance - capable of weighing accurately to ± 0.001 g
- ASTM Class 1 weights
- Desiccator
- Drying oven, capable of being controlled at 105 ± 5°C
- Stirrer Plate and Stirring Bars

### 7.2 Reagents

Reagents may contain impurities that affect analytical data. Only materials that conform to the American Chemical Society (ACS) reagent grade specifications should be used. If the purity of a reagent is in question, analyze for contamination prior to use.

Record all chemical and reagent preparations in the LIMS database. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

- Reagent water - As defined in USEPA Region 9 Laboratory SOP 825, *Deionized Water*.
- Degassed reagent water - Reagent water that has been purged with helium or nitrogen for at least 2 minutes.

- Blank solid matrix - Acid washed sand
- Sodium bicarbonate ($NaHCO_3$), ACS reagent grade
- Sodium carbonate ($Na_2CO_3$), ACS reagent grade
- Sodium bromide (NaBr), ACS reagent grade
- Sodium chloride (NaCl), ACS reagent grade
- Sodium fluoride (NaF), ACS reagent grade
- Sodium nitrate ($NaNO_3$), ACS reagent grade
- Sodium nitrite ($NaNO_2$), ACS reagent grade
- Potassium phosphate ($KH_2PO_4$), ACS reagent grade
- Potassium sulfate ($K_2SO_4$), ACS reagent grade
- Helium, ultra high purity grade (UHP)
- Nitrogen

7.2.1 Eluent Stock Solutions

- 0.5 M Sodium Carbonate

  Prepare by dissolving 26.49 g of sodium carbonate in 400 mL of reagent water and diluting to final volume of 500 mL, or equivalent purchased commercially (e.g.; Dionex).

- 0.5 M Sodium Bicarbonate

  Prepare by dissolving 8.40 g of sodium bicarbonate in 100 mL of reagent water and diluting to final volume of 200 mL, or equivalent purchased commercially (e.g.; Dionex).

7.2.2 Eluent Working Solution, 8 mM $Na_2CO_3$ / 1 mM $NaHCO_3$

Prepare working eluent solution by pipetting 32 mL of 0.5 M $Na_2CO_3$ and 4 mL of 0.5 M $NaHCO_3$ into a 2-L volumetric flask and diluting to volume with degassed reagent water.

7.3 Standards

Record all standard and standard preparations in the LIMS database.

7.3.1 Stock Standards

Stock standard solutions may be purchased as certified solutions (ex.: 1,000 mg/L from Inorganic Ventures) or prepared from ACS reagent grade materials (dried at 105 °C for 30 minutes) and are stable for at least a year when stored at 4 °C. The stock standards are also used to make calibration and quality control standards as needed.

- 1,000 mg/L Fluoride standard is prepared by dissolving 1.105 g NaF in reagent water to a final volume of 500 mL.

- 1,000 mg/L Chloride standard is prepared by dissolving 0.824 g of NaCl in reagent water to a final volume of 500 mL.

- 1,000 mg/L Nitrite-N standard is prepared by dissolving 2.463 g $NaNO_2$ in reagent water to a final volume of 500 mL.

- 1,000 mg/L Bromide standard is prepared by dissolving 0.644 g NaBr in reagent water to a final volume of 500 mL.

- 1,000 mg/L Nitrate-N standard is prepared by dissolving 3.034 g $NaNO_3$ in reagent water to a final volume of 500 mL.

- 1,000 mg/L Orthophosphate-P standard is prepared by dissolving 2.197 g of $KH_2PO_4$, in reagent water to a final volume of 500 mL.

- 1,000 mg/L Sulfate standard is prepared by dissolving 0.9070 g of $K_2SO_4$ in reagent water to a final volume of 500 mL.

7.3.2 Working Standards

Intermediate standards may be prepared and used to make calibration and quality control standards as needed.

- 100 mg/L Fluoride and Bromide

  Prepare by adding 50 mL each of the 1,000 mg/L F and Br into a 500-mL volumetric flask and diluting to volume with reagent water.

- 100 mg/L Nitrite-N and Nitrate-N

  Prepare by adding 50 mL each of the 1,000 mg/L $NO_2$-N and $NO_3$-N into a 500-mL volumetric flask and diluting to volume with reagent water.

- 250 mg/L Chloride, Orthophosphate-P, and Sulfate

  Prepare by adding 50 mL each of the 1,000 mg/L Cl, O-$PO_4$-P, and $SO_4$ into a 200-mL volumetric flask and diluting to volume with reagent water.

7.3.3 Calibration Standard 6 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 10 | 5 mL of 100 mg/L F and Br | 50 |
| Bromide | 10 | | |
| Nitrite-N | 25 | 12.5 mL of 100 mg/L $NO_2$-N and $NO_3$-N | |
| Nitrate-N | 25 | | |
| Chloride | 50 | 10 mL of 250 mg/L Cl, O-$PO_4$-P, and $SO_4$ | |
| o-Phosphate-P | 50 | | |
| Sulfate | 50 | | |

7.3.4 Calibration Standard 5 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 2.0 | 1 mL of 100 mg/L F and Br | 50 |
| Bromide | 2.0 | | |
| Nitrite-N | 10 | 5 mL of 100 mg/L $NO_2$-N and $NO_3$-N | |
| Nitrate-N | 10 | | |
| Chloride | 25 | 5 mL of 250 mg/L Cl, O-$PO_4$-P, and $SO_4$ | |
| o-Phosphate-P | 25 | | |
| Sulfate | 25 | | |

7.3.5 Calibration Standard 4 / CCV / LCS - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 1.0 | 1 mL of 100 mg/L F and Br | 100 |
| Bromide | 1.0 | , , | |
| Nitrite-N | 5.0 | 5 mL of 100 mg/L $NO_2$-N and $NO_3$-N | |
| Nitrate-N | 5.0 | | |
| Chloride | 10 | 4 mL of 250 mg/L Cl, | |

| | | |
|---|---|---|
| | | $O\text{-}PO_4$-P, and $SO_4$ |
| o-Phosphate-P | 10 | |
| Sulfate | 10 | |

7.3.6 Calibration Standard 3 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 0.5 | 0.25 mL of 100 mg/L F and Br | 50 |
| Bromide | 0.5 | | |
| Nitrite-N | 1.0 | 0.5 mL of 100 mg/L $NO_2$-N and $NO_3$-N | |
| Nitrate-N | 1.0 | | |
| Chloride | 5.0 | 1 mL of 250 mg/L Cl, $O\text{-}PO_4$-P, and $SO_4$ | |
| o-Phosphate-P | 5.0 | | |
| Sulfate | 5.0 | | |

7.3.7 Calibration Standard 2 - Dilute working standards (Section 7.3.2) to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 0.25 | 0.125 mL of 100 mg/L F and Br | 50 |
| Bromide | 0.25 | | |
| Nitrite-N | 0.5 | 0.25 mL of 100 mg/L $NO_2$-N and $NO_3$-N | |
| Nitrate-N | 0.5 | | |
| Chloride | 1.0 | 0.2 mL of 250 mg/L Cl, $O\text{-}PO_4$-P, and $SO_4$ | |
| o-Phosphate-P | 1.0 | | |
| Sulfate | 1.0 | | |

7.3.8 Calibration Standard 1 - Dilute working standards (Section 7.3.2) or working standard to volume with reagent water as shown in the following table. Prepare daily.

| *Analyte* | *Final Concentration, mg/L* | *Volume of Working Standard* | *Final Volume, mL* |
|---|---|---|---|
| Fluoride | 0.1 | 0.05 mL of 100 mg/L F and Br | 50 |

| | | |
|---|---|---|
| Bromide | 0.1 | |
| Nitrite-N | 0.1 | 0.05 mL of 100 mg/L $NO_2$-N and $NO_3$-N |
| Nitrate-N | 0.1 | |
| Chloride | 0.5 | 0.1 mL of 250 mg/L Cl, O-$PO_4$-P, and $SO_4$ |
| o-Phosphate-P | 0.5 | |
| Sulfate | 0.5 | |

7.3.9 QLS

Pipet 0.05 mL of the 100 mg/L F, Br, $NO_2$-N, and $NO_3$-N working standard, 0.05 mL of the 1,000 mg/L chloride and orthophosphate-P stock standard, and 0.025 mL of 1,000 mg/L sulfate stock standard into a 50-mL volumetric flask and dilute to volume with reagent water. Prepare daily. QLS concentrations are shown in the following table:

| *Analyte* | *Concentration, mg/L* |
|---|---|
| Fluoride | 0.10 |
| Chloride | 1.0 |
| Nitrite-N | 0.10 |
| Bromide | 0.10 |
| Nitrate-N | 0.10 |
| o-phosphate-P | 1.0 |
| Sulfate | 0.50 |

7.3.10 SCV

Prepare or obtain an SCV from a source external to the laboratory and different from the source of the calibration standards. A Multi-Anion solution from Alltech is available in the concentrations shown in the following table. Dilute by a factor of four prior to analysis to get all analytes within calibration range.

| *Analyte* | *Concentration, mg/L* |
|---|---|
| Sulfate | 30 |
| Bromide | 20 |
| Chloride | 20 |
| Fluoride | 10 |
| o-Phosphate-P | 10 |
| Nitrite-N | 6.0 |
| Nitrate-N | 4.5 |

7.4 Supplies

- Clean sand (used as a blank for solid matrix)
- 100-mL beakers or Erlenmeyer flasks
- Disposable beaker cups
- Disposable syringe filters, 0.20-micron and 0.45-micron
- Disposable syringes with Luer-lock fittings
- Plastic or Teflon spray bottle
- Polyvials, 5 mL capacity with filter caps (Dionex P/N 38141)
- Volumetric Class A Flasks - 2000 mL, 500 mL, 100 mL, 50mL, 25ml, and 10mL
- Volumetric Class A Pipettes - 10 mL, 5 mL, and 4 mL

## 8 ANALYTICAL PROCEDURES

### 8.1 Instrument Operation

Set-up the ion chromatograph following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix D as a starting point. Appendix E provides instrumental startup information.

Ensure that all appropriate waste containers are properly connected and labeled. Ensure that waste containers will not overflow.

### 8.2 Calibration and Standardization

#### 8.2.1 Initial Calibration

Perform an initial calibration using a minimum of six calibration standards to establish a quadratic curve. Analyze calibration standards as described in Section 8.3.3. Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Analyze a calibration blank immediately after the initial calibration. If the value of the CB is less than one-half the QL, the calibration is acceptable. If the value of the blank result equals or exceeds one-half the QL, the cause of the high CB result must be determined, the problem corrected, and the instrument re-calibrated.

Analyze an SCV standard to confirm the initial calibration. Meet QC criteria and take corrective action as needed as described in Section 9.2.1 and Appendix C.

NOTE: Update retention time windows in the instrument software after each initial calibration. Five percent of Standard 4 retention times should generally

be used to define calibration retention time windows. Print a record of the retention time windows and retain for inclusion in the data package.

8.2.2 Continuing Calibration Verification

At the beginning of each analytical sequence, verify calibration with a CCV standard. Prepare the CCV as described in Section 7.3.4 and analyze according to Section 8.3. Follow requirements and take corrective action as described in Section 9.2.2.

NOTE: After the first CCV analysis, update retention times in the instrument software to correspond to the first CCV and adjust retention time window to 5% of the retention times.

8.3 Analysis

8.3.1 Water Sample Preparation

1. Prepare MS and MSD samples by fortifying the source sample with primary stock or working standards. The MS/MSD spike levels in the following table are recommended for most projects:

| *Parameter* | *Recommended MS/MSD Spiking Levels, mg/L* |
|---|---|
| Fluoride | 1 |
| Chloride | 10 |
| Nitrite-N | 5 |
| Bromide | 1 |
| Nitrate-N | 5 |
| o-Phosphate-P | 10 |
| Sulfate | 10 |

2. Filter samples that are turbid or contain particulates to prevent damage to instrument columns and flow systems. Filter samples following this procedure:

   Transfer an aliquot of a well-mixed unfiltered sample into a disposable beaker cup. Draw approximately 5 mL of the sample into a disposable syringe. Attach a 0.45-micron disposable syringe filter to the syringe. Apply pressure to the plunger and filter the sample through the syringe filter and into a 5-mL vial. Repeat the procedure until the 5-mL vial is filled close to the 5-mL mark. Discard the remaining sample from the beaker cup into the liquid waste container and the syringe assembly into a solid waste container.

If sample is still turbid or colored, filter the sample again following the procedure above using the 0.20-micron disposable syringe filter.

NOTE: A separate MB must be filtered if any sample in the batch is filtered. Use corresponding filter that was used for the sample. Record any sample filtrations in the comments section of the LIMS benchsheet.

3. Fill 5-mL polyvials with each well-mixed sample. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it is flush with the top of the vial. Label the contents of the vial.

8.3.2 Solid Sample Preparation

1. For homogenization of solid samples, follow SOP 150, *Soil and Sediment Homogenization.*

2. Weigh out approximately 2.0 g of each solid sample. Sample weights may be adjusted to meet project requirements, if necessary. Add reagent water equal to ten times the weight of solid material taken as sample. (Example: To 2.2 g of solid sample, add 22 mL of reagent water).

3. Prepare MS, MSD, and LCS samples. For MS and MSD samples, fortify the source sample with primary stock or working standards. Prepare the LCS by fortifying a blank solid matrix with primary stock or working standards. The following table provides MS/MSD and LCS spike levels suitable for most projects:

| *Parameter* | *Recommended MS/MSD & LCS Spiking Levels, mg/L* |
|---|---|
| Fluoride | 1 |
| Chloride | 10 |
| Nitrite-N | 5 |
| Bromide | 1 |
| Nitrate-N | 5 |
| o-Phosphate-P | 10 |
| Sulfate | 10 |

4. Mix each sample with a shaker table or a magnetic stirrer for 10 to 15 minutes. Filter the resulting mixture with a 0.45-micron or 0.20-micron filter as described in Section 8.3.1.

5. Fill 5-mL polyvials with each well-mixed sample filtrate. Attach a filter cap to each vial and push down the filter cap with the supplied tool until it

is flush with the top of the vial. Label the contents of the vial.

6. From a separate sample aliquot, determine moisture following SOP 460, *Percent Solids Determination*.

8.3.3 Analytical Sequence and Sample Analysis

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument software and the LIMS sequence.

Include all batch QC samples as described in Section 9.3.

1. Enter sample sequence in the instrument software. (Refer to Appendix E for details regarding entering the sequence). Load the samples to be analyzed in the autosampler according to their designated positions in the sequence file.

2. The following table shows an example of a typical sample sequence. If not calibrating the instrument, start with Seq. #9.

| *Seq.* | *Description* | *Seq.* | *Description* | *Seq.* | *Description* |
|---|---|---|---|---|---|
| 1 | Cal Std 1 | 15 | S1-MS ** | 29 | S12 |
| 2 | Cal Std 2 | 16 | S1-MSD ** | 30 | S13 |
| 3 | Cal Std 3 | 17 | S2 | 31 | S14 |
| 4 | Cal Std 4 | 18 | S3 | 32 | S15 |
| 5 | Cal Std 5 | 19 | S4 | 33 | CCV |
| 6 | Cal Std 6 | 20 | S5 | 34 | CB |
| 7 | CB | 21 | CCV | 35 | S16 |
| 8 | SCV | 22 | CB | 36 | S17 |
| 9 | CCV/LCS | 23 | S6 | 37 | S18 |
| 10 | CB/MB | 24 | S7 | 38 | S19 |
| 11 | QLS * | 25 | S8 | 39 | S20 |
| 12 | MB (for filtered or solid samples) | 26 | S9 | 40 | CCV |
| 13 | LCS (for solid samples) | 27 | S10 | 41 | CB |
| 14 | S1 | 28 | S11 | 42 | |

* A QLS must be analyzed daily at the beginning of the analytical run and every subsequent 40 analytical samples.
** Alternatively, analyze MD as specified in Section 9.3.4.

3. If any water sample is filtered, analyze a separate filtered MB. If no sample is filtered, the CB serves as the MB.

4. Start the autosampler (Dionex AS40) by pressing the 'Hold/Run' button until the light on the side of the word 'Run' is lighted. Initiate the analysis by clicking on the 'Start' button in the Batch list section of the software. The analysis will stop automatically by inserting a 'Sample' positioned at the end of the sequence file and changing the Program name (Anions Program) under the 'Program' column to 'StopMethod', and re-saving the edited sequence file.

5. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

6. If the water dip interferes with the fluoride peak, try the following:

   - Optimize instrument condition to maximize fluoride peak resolution.
   - If using an old column, clean or replace the analytical column.
   - If the first two steps fail, add the equivalent of 1 mL of concentrated eluent (100x) to 100 mL of each standard and sample.

8.3.4 Analyte Identification and Quantitation

8.3.4.1 Peak Identification

Review all chromatograms to ensure that the correct peaks are integrated. The instrument is typically set to identify peaks as target analytes if the retention times are within ± 5% of retention times from the first CCV.

8.3.4.2 For water samples, report results in mg/L using the following equation:

$$C = M \, x \, D$$

Where
$C$ = final reported concentration, in mg/L
$M$ = measured concentration reported by software, in mg/L
$D$ = sample analysis dilution factor, to account for any dilution

8.3.4.3 For solid samples, report results in mg/kg using the following equation:

$$C = M \times \frac{Vf}{Vi} \times D \times 100 / S$$

Where

$C$ = final reported concentration, in mg/kg
$M$ = measured concentration reported by software, in mg/L
$V_f$ = final volume of sample solution after sample preparation, in liters
$V_i$ = initial weight of sample used in sample preparation, in kilograms
$D$ = sample analysis dilution factor, to account for any dilution
$S$ = percent of solids in the sample used

8.3.4.4 Nitrite results in the presence of chloride

Quantitation of nitrite may be affected by the chloride concentration. Therefore, apply the following rules:

- For undiluted samples where nitrite is not detected, report nitrite as follows:

  1. If chloride concentration ≤50 mg/L, report nitrite QL = 0.1 mg/L.
  2. If chloride concentration >50 mg/L, dilute and reanalyze sample. In this case, the nitrite QL is 0.1 mg/L multiplied by the dilution factor used for chloride analysis.

- For undiluted samples where nitrite is present, nitrite must be reported regardless if chloride is detected. Report nitrite as follows:

  1. If nitrite is present from 0.05 mg/L to 0.09 mg/L, report result as estimated (J).
  2. If nitrite is present from 0.1 mg/L to 0.25 mg/L and chloride is ≤100 mg/L, report nitrite result without qualification. If chloride is >100 mg/L and <400 mg/L, the nitrite result is estimated with low bias (L) due to interference from chloride.
  3. If nitrite is present at >0.25 mg/L to ≤0.5 mg/L and chloride is ≤200 mg/L, report nitrite without qualification. If chloride is >200 mg/L to ≤400 mg/L, the nitrite result estimated with low bias (L) due to interference from chloride.
  4. If nitrite is present at >0.5 mg/L, report without qualification.

8.3.4.5 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be

stamped, initialed and dated by the analyst, and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.5 Data and QC Review

- Review results of instrument QC (CCV, CB, QLS) immediately after their analysis to verify that the results are within QC limits. See Section 9.2 for corrective action requirements and Appendix C for QC limits.

- Review results of batch QC (MB, LCS, MS/MSD/MD). See Section 9.3 for corrective action requirements and Appendix C for QC limits.

8.3.6 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS. The LIMS will report two significant figures and detected results to one-half the QL. The LIMS will flag values between one-half the QL and the QL as estimated (J). The analyst must manually add a qualifier flag (C1) indicating that the reported concentration is estimated because it is less than the quantitation limit. Qualify data based on QC results and guidelines in the EPA Region 9 Laboratory QA Plan.

8.4 Maintenance

Column maintenance prolongs column life and reduces retention time shifts. Shorter retention time and smaller peaks are indications that a column is degrading and maintenance is necessary. Refer to manufacturer's requirements for column maintenance.

Monitor retention time shift. Retention time drift, as indicated by the first CCV, of >5% is an indication that instrument maintenance may need to be performed.

Routine instrument maintenance is summarized in Appendix F.

## 9 QUALITY CONTROL

The EPA Region 9 Laboratory operates a formal quality control program and tracks compliance using the Lab QC Database. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

The following sections describe quality control measures, criteria, frequency, and corrective action. Appendix C summarizes QC measures and criteria.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880, *Demonstration of Capability*.

9.2 Instrument QC

9.2.1 Initial Calibration

An initial calibration is performed by analysis of a minimum of six standards. Calibration for all analytes is calculated using a quadratic fit. The coefficient of determination for the initial calibration must be $\geq 0.995$ for the calibration to be valid. The calibration is verified by analyzing a SCV standard. Refer to Appendix C for acceptance criteria.

If an ICAL fails because of one standard, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If the calibration does not meet coefficient of determination and SCV criteria, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

9.2.2 Continuing Calibration Verification

To check instrument performance and verify the accuracy and stability of the calibration, analyze a CCV standard. The CCV is analyzed prior to analyzing each analytical batch, at a frequency of one per 10 analytical samples, and at the end of the analytical run.

The recovery of analytes in the CCV is calculated as follows:

$$\%R = \frac{M}{T} \times 100$$

Where

$\%R$ = percent recovery of the standard
$M$ = measured concentration of analyte, mg/L

$T$ = true concentration of the analyte in the CCV, mg/L

If the CCV recovery is not within QC criteria, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the poor recovery must be determined and the problem corrected. All samples not bracketed by acceptable CCV results must be reanalyzed.

NOTE: If it is suspected that the CCV was prepared incorrectly, it may be re-prepared and reanalyzed. If it passes, the analysis may continue.

9.2.3 Calibration Blank

The stability of the baseline must be monitored by analyzing a CB immediately after everyCCV standard. If the value of the CB result is less than ½ the QL, the result is acceptable. If the value of the CB result equals or exceeds ½ the QL, the analysis may continue but samples cannot be analyzed for the out-of-control analytes. The cause of the high CB result must be determined and the problem corrected. All samples not bracketed by acceptable CB results must be reanalyzed.

NOTE: If it is suspected that there is contamination in the vial used for the CB, the blank may be re-poured and reanalyzed. If it passes, the analysis may continue.

9.2.4 Quantitation Limit Standard

To verify the ability to detect target analytes near the QL, a QLS must be analyzed at the beginning of the analytical run (typically just after the CCV and CB) and every subsequent 40 analytical samples.

The recovery of analytes in the QLS is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where
%R = percent recovery of the standard
$M$ = measured concentration of the analyte, mg/L
$T$ = true concentration of the analyte in the QLS, mg/L

If the QLS recovery does not meet criteria in Appendix C, determine the cause, take corrective action, and reanalyze the QLS.

NOTE: Any samples analyzed in an autosampler sequence after a failing QLS must be reanalyzed after the system has been corrected and the standard meets acceptance criteria

9.3 Batch QC

9.3.1 Method Blank

Analyze one MB with each batch of 20 or fewer field samples of the same matrix. MB values ≥ ½ QL indicate potential laboratory or reagent contamination. Use the following guidelines to determine when samples must be re-prepared and reanalyzed:

a) If the MB analyte value ≥ ½ QL and the sample result is less than five times the MB analyte amount, rerun the MB once to verify and if still unacceptable then the MB and all associated samples must be re-prepared and reanalyzed. If either the holding time is expired or no more sample volume is available, the associated sample results may be reported but will be qualified as estimated "J" and a note must be entered in the Work Order Memo field explaining the situation.

b) If the MB analyte value ≥ ½ QL and the sample result is non-detected or is greater than or equal to five times the MB analyte concentration, report sample results without qualification.

NOTE: The first CB analyzed meets the requirement of the MB if no sample preparation was performed. If sample preparation was performed (e.g. filtration), a filtered MB must be prepared and analyzed separately.

9.3.2 LCS

Analyze one LCS with each batch of 20 or fewer field samples of the same matrix. NOTE: For analysis of water samples, the LCS is equivalent to a CCV. Analysis of a CCV serves as both a CCV and the batch LCS.

LCS recovery is calculated as:

$$\%R = \frac{Cm}{Ct} \times 100$$

Where
$\%R$ = percent recovery
$C_m$ = measured analyte concentration in the LCS
$C_t$ = true analyte concentration in the LCS

If the LCS recovery does not meet recovery criteria, reanalyze once to verify, if still does not meet criteria provided in Appendix C, determine the cause, take corrective action, and reanalyze all samples associated with the out-of-control LCS. If either the holding time is expired or no more sample volume is available, the associated sample results may be reported but will be qualified as estimated "J", in this case a note must be entered in the Work Order Memo field explaining the situation.

9.3.3 Matrix Spike/Matrix Spike Duplicate

The MS and MSD are designed to provide information about the effect of sample matrix on the measurement system. One set of MS/MSD samples must be analyzed for each 20 or fewer field samples of the same matrix in an SDG. If the analyte concentration of the MS/MSD source sample is more than four times the MS/MSD spike level, an MD sample is analyzed and reported instead of the MS/MSD samples.

Samples identified as field blanks cannot be used for MS and MSD sample analysis. MS/MSD recoveries are calculated as:

$$\%R = \frac{Cms - C}{s} \times 100$$

Where

$\%R$ = percent recovery
$C_{ms}$ = measured concentration of analyte in the MS, corrected for sample preparation and any dilutions
$C$ = measured concentration of analyte in the routine sample corrected for sample preparation and any dilutions
$s$ = expected spiked analyte concentration in the MS, corrected for sample preparation and any dilutions

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmsd - Cms|}{(Cmsd + Cms)/2} \times 100$$

Where

$RPD$ = relative percent difference
$C_{msd}$ = measured concentration in the MSD, corrected for sample preparation and any dilutions
$C_{ms}$ = measured concentration in the MS, corrected for sample preparation and any dilutions

If the value of $C$ is less than four times the value of $s$, apply accuracy and precision criteria in Appendix C. If the MS/MSD does not meet the acceptance criteria, examine other QC results to determine if a matrix problem exists. If laboratory performance is in control, the poor MS/MSD accuracy or precision is likely to be matrix-related. Flag any out-of-control results as estimated (J).

9.3.4 Matrix Duplicate

Sample homogeneity can affect the quality and interpretation of the data. MD results can be used to assess sample homogeneity.

A matrix duplicate is analyzed only if the original sample concentration is more than four times the matrix spike level. A sample and a matrix duplicate are diluted, if needed, and analyzed for every MS and MSD that falls outside of the calibration range.

Calculate the relative percent difference (RPD) using the following equation:

$$RPD = \frac{|Cmd - C|}{(Cmd + C)/2} \times 100$$

Where

$RPD$ = relative percent difference
$C_{md}$ = measured concentration in the MD, corrected for sample preparation and any dilutions
$C$ = measured concentration in the routine sample, corrected for sample preparation and any dilutions

The RPD for any analyte must be $\leq 20$ for samples with analyte levels $\geq$ QL. If the control limits are exceeded, flag all associated analyte results as estimated (J).

9.4 Method Performance

The following table summarizes method performance by matrix for the period 04/01/2012 to 05/03/2013.

| | | Method Performance | | |
|---|---|---|---|---|
| *Analyte* | *Matrix* | *Number of Measurements* | *Mean Recovery, %* | *95% Confidence Interval (2σ)* |
| Fluoride | Water | 109 | 95.6 | 83.2 - 108 |
| Chloride | Water | 109 | 96.5 | 90.8 - 103 |
| Nitrite-N | Water | 109 | 97.2 | 89.9 - 105 |
| Bromide | Water | 109 | 98.7 | 88.6 - 109 |

| *Analyte* | *Matrix* | *Number of Measurements* | *Mean Recovery, %* | *95% Confidence Interval (2σ)* |
|---|---|---|---|---|
| Nitrate-N | Water | 109 | 98 | 91 - 105 |
| Orthophosphate-P | Water | 109 | 98.6 | 89.9 - 107 |
| Sulfate | Water | 109 | 99.9 | 90.4 - 110 |

The primary sources of analytical error are:

- Analytical balance
- Instrument calibration
- Pipette calibration
- Standard's accuracy
- Vial contamination

## 10 DOCUMENTATION

### 10.1 Standards

All standards (ICAL, CCV, QLS, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis must be included in the data package.

### 10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

### 10.3 Analytical sequence

The analytical sequence is documented in the Element database or in the instrument sequence Log. Project Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

### 10.4 Analytical Report and Data Package

Analytical reports are produced using the Element database. The data package is produced from Element database and manual log records. Appendix G provides the typical format for data package deliverables.

### 10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance.
- Subsequent instrument modifications and upgrades, including major software upgrades.
- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with EPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Read and Understood

After approval, distribute an electronic copy of the final SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. (The Lab QC Database contains a list of assigned analysts for each SOP). All approved EPA Region 9 Laboratory SOPs are maintained in the LotusNotes database in Adobe Acrobat portable document format.

Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Laboratory QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

## 11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on LotusNotes or the local area network (G:\USER\SHARE\QA PROGRAM\LAB SOPS PDF) for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

U.S. Environmental Protection Agency, 1993. *EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1.*

## APPENDIX A.
## DEVIATIONS FROM THE REFERENCE METHOD

1. The scope of the SOP does not include the analysis of bromate, chlorate, chlorite, and sulfite.

2. The SOP requires that the MB be less than one-half the QL, while the reference method specifies that MB be less than the MDL. Region 9 Laboratory policy specifies that results be reported to one-half the QL.

3. The SOP specifies sample storage temperature of > 0 to ≤ 6 °C, while the reference method specifies 4 °C.

4. The SOP calculates the width of the retention time window used to make identifications based on ± 5% of the first CCV retention times. The reference method states that the width of the retention time window should be determined using three times the standard deviation of measurements of actual retention times of standards over the course of a day.

5. The SOP specifies six concentration levels and a quadratic fit for calibration, as recommended by the instrument manufacturer, while the reference method recommends a minimum of three concentration levels and a linear curve fit.

6. To improve chromatographic separation, the SOP specifies the working eluent solution to be 8 mM $Na_2CO_3$ / 1 mM $NaHCO_3$, while the reference method specifies it to be 1.8 mM $Na_2CO_3$ / 1.7 mM $NaHCO_3$.

7. The SOP uses the SCV standard to meet the requirements of the QCS specified in the reference method. While the method requires the QCS to be analyzed quarterly, the SOP requires an SCV standard be analyzed with each initial calibration, which may be more or less frequent than quarterly.

8. The SOP specifies MS/MSD recovery criteria to be 80 - 120%. The reference method specifies the initial limits to be 90 - 110% and allows 80 - 120% if control charts are used.

9. The reference method specifies that matrix QC frequency be prepared to a minimum of 10 percent of the routine samples; this SOP conforms to EPA Region 9 Laboratory policy for matrix QC frequency.

## APPENDIX B.
## ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

| *Analyte* | *Chemical Abstracts Registry Number (CASRN)* | *Water Quantitation Limit, mg/L* | *Soil Quantitation Limit, mg/kg* |
|---|---|---|---|
| Fluoride | 7681-49-4 | 0.1 | 1 |
| Chloride | 7647-14-5 | 1 | 10 |
| Nitrite-N | 7632-00-0 | 0.1 | 1 |
| Bromide | 7647-15-6 | 0.1 | 1 |
| Nitrate-N | 7631-99-4 | 0.1 | 1 |
| Orthophosphate-P | 7778-77-0 | 1 | 10 |
| Sulfate | 7778-80-5 | 0.5 | 5 |

# APPENDIX C.
# QUALITY CONTROL MEASURES AND CRITERIA

| *Parameter* | *Frequency* | *Criteria* |
|---|---|---|
| Coefficient of Determination | Each ICAL | ≥ 0.995 |
| SCV | After ICAL | 90 - 110% |
| CCV | Beginning, every 10 samples, and end of run | 90 - 110% |
| CB | After every CCV | < ½ QL |
| QLS | Beginning and every subsequent 40 analytical samples | 60 - 140% |
| MB | Each batch of 20 or fewer samples | < ½ QL |
| LCS | Each batch of 20 or fewer samples | 90 - 110% |
| MS/MSD, accuracy | Every 20 or fewer samples in an SDG | 80 - 120% |
| MS/MSD, MD precision | Every 20 or fewer samples in an SDG | ≤ 20 RPD |
| CCV Retention Time Drift | Each batch | ± 5% ICAL Std 4 |
| Retention Time Window | Each batch | ± 5% first CCV |

# APPENDIX D.
# TYPICAL ION CHROMATOGRAPH OPERATING PARAMETERS

General Parameters
Dimension of amounts: mg/L
Global Calibration Settings: Total
Auto Recalibrate: Select
Use Recently Detected Retention Times: Deselect
Reference Inject Volume: Fixed, 25.0 µL
Blank Run and Matrix Blank: No blank run subtraction

Detector Parameters
Detector Type: conductivity
Data Collection time (minutes): 13.5 for ICS1100; 12.0 for ICS2500
Data Collection Rate: 5.00 Hz
Real time plot scale maximum (µs): 15,100 for ICS1100; 3,000 for ICS2500

ICS1100 Integration Detection Parameters

| Time | Description |
|---|---|
| 0.00 | Min. Area 0.003 "[Signal]*min" |
| 0.00 | Inhibit Integration ON |
| 0.00 | Peak Slice 1.50 s |
| 0.00 | Fronting Sensitivity Factor 4.0 |
| 2.3 | Sensitivity 0.004 "[Signal]" |
| 2.6 | Tailing Sensitivity Factor 10.0 |
| 2.6 | Minimum Height 0.0175 "[Signal]" |
| 2.6 | Valley to Valley On |
| 2.6 | Inhibit Integration OFF |

ICS2500 Integration Detection Parameters

| Time | Description |
|---|---|
| 0.00 | Min. Area 0.002 "[Signal]*min" |
| 0.00 | Inhibit Integration ON |
| 0.00 | Peak Slice 0.50 s |
| 2.30 | Valley to Valley On |
| 2.30 | Inhibit Integration OFF |
| 2.30 | Sensitivity 0.004 "[Signal]" |
| 2.30 | Fronting Sensitivity Factor 10.0 |
| 2.30 | Tailing Sensitivity Factor 7.0 |
| 2.30 | Minimum Height 0.015 "[Signal]" |

NOTE: The sensitivity and the minimum area values may change overtime depending on baseline noise for both ICS1100 and ICS2500.

Calibration Parameters
External or internal calibration: EXTERNAL
Number of replicates for calibration: 1
Update response: Yes
Default dilution factor: 1.00
Default response factor for unknown peaks: 0.00
Calculate unknowns by area or height: Area
Calibration Fit: Quadratic
Flow Rate, initial setup: 1.2 mL/min, adjust as needed.

# APPENDIX E.
# TYPICAL STARTUP PROCEDURES

## TYPICAL STARTUP PROCEDURE FOR THE ICS1100

1. Ensure that the helium and nitrogen regulator on the system is set at 5 ±1 psi and gas is on.

2. Turn on the computer system and printer connected to the instrument. Log into the network. Double click on the 'Server Monitor' icon and click on the 'Start' button to turn on the Chromeleon server. This will allow the instrument to transfer data into the computer. When the server is running, the message in the status box on the computer monitor should display "Chromeleon Server is running idle".

3. Double click on the 'Chromeleon' icon and find the 9L1207HWFM51_Local directory. Click on the ICS1100 and double click on ICS1100 pts. Maximize the screen by clicking on a "square box with arrows on each corner" icon.

   Click on Pump Settings and enter 1.2 mL/min on the flow rate box and click on the ON button. Then click CLOSE button.

   Click on the Detector Settings and enter 51 mA in the box for the suppressor current, press 'Enter' on the computer keyboard and then click on CLOSE button.

   The system pressure is typically around 2,000 psi and the baseline conductivity reading should be around 24 µS.

4. Open the browser section of the multi colored (red, blue, green, and yellow) button at the top of the control panel by clicking on it. Set up a sequence by clicking on a sequence file that contains the last calibration performed on the instrument. The sequence files are located in: C:\Chromel\9L207HWFM51_Local\ICS1100\Data\Year_Anions\[*sequence#*]

   The sequence number is a seven digit number containing the last two digit of the year, the month, the day, and the run number, ex. 1108191. Re-save the accessed file and save it as today's sequence file. Ensure that the small box 'Save Raw Data' is checked on prior to clicking the save button. Under the 'Status' column for each position to be analyzed in the sequence, change 'Finished' to 'Single'. This will enable the computer system to acquire the data for the standards and samples to their designated position in the sequence file. Ensure that the 'Status' column for the calibration standards (std1 thru std6) says 'Finished', which will prevent the computer from writing over the calibration data. If a new calibration is to be analyzed with the QC standards and samples, every entry in the 'Status' column should be 'Single'. Check for errors within the sequence file by clicking on 'Batch', 'Edit', 'Add', click on the sequence file you wish to run, click 'Open', click on the data file that was just added, click on 'Ready Check', when it says 'OK', click on the 'OK' box. Then click on the 'Start' button to start the analytical sequence.

## TYPICAL STARTUP PROCEDURE FOR THE ICS2500

1. Ensure that the helium or nitrogen regulator on the system is set at approximately at 5 ±1 psi and the gas is on.

2. Follow step #1 on the ICS1100 startup procedure.

3. Double click on the 'Chromeleon' icon and find the C:\Chromel\9L207HWFM51_Local\Data\Year_Anions\ directory. Double click on the last analytical sequence and double click on the 'Conductivity_A_Detector_Gradient_Pump_AS40_LC30.pan' panel and click on 'Connect', if not connected.

4. Turn the eluent on by clicking on the 'ON' button on the control panel. Set the oven temperature to 30°C by typing in '30' on the space beside the word 'Oven Temperature' and press 'Enter' on the computer keyboard. Then turn on the SRS current by typing in '51' mA in the space beside the word 'Current' and press 'Enter' on the computer keyboard. The system pressure is typically 2200 psi and the baseline conductivity at approximately 25 uS.

5. Follow step #4 on the ICS1100 startup procedure except the sequence files for the ICS2500 are located in: C:\Chromel\9L207HWFM51_Local\ICS2500\Data\Year_Anions\[*sequence#*]

# APPENDIX F.
# PREVENTATIVE MAINTENANCE REQUIREMENTS

Maintenance Schedule for the ICS1100 and the ICS2500

| Item | Frequency | Comments |
|---|---|---|
| Eluent Filter | As needed | Check filters for discoloration when preparing fresh eluent from new stocks, replace if needed. |
| Eluent Reservoir | As needed | Wash the reservoir thoroughly when preparing fresh eluent from new stocks. |
| Pump | Daily | Prime prior to starting the instrument to prevent air bubbles from entering columns. |
| High System Pressure | As needed | Check individual pressure of guard and analytical columns. |
| Guard Column | As needed | Condition guard column if pressure is more than ¼ of the analytical column, if still high, replace.<br>If a false positive o-phosphate peak appears in the blank, replace the inlet frit on the guard column. If the o-phosphate peak persists, clean the guard column. If the o-phosphate still persists, replace the guard column. |
| Analytical Column | As needed | Condition analytical column if pressure is more than 4 times of the guard column, if still high replace. |
| Low System Pressure and/ or Leak Alarm | As needed | Tighten or replace leaky lines or fittings. |
| Piston/pump seals and o-ring in pump head | Annually | Replace |
| Inlet frit of guard column | As needed | Replace if system pressure has increased by more than 200 psi and there's solid residue on frit. |
| Suppressor | As needed | Replace if peak resolutions are not well defined and the baseline noise interfere with peak quantitation. |
| Check valves | Annually | Replace |
| Injection Valve | Annually | Rebuild with new rotor seal and stator phase. |
| Autosampler tip assembly | Annually | Replace |

# APPENDIX G.
# TYPICAL DATA PACKAGE FORMAT

Data package contents, in order. Optional sections are shown in *italic text*. Separator pages are underlined.

ESAT Cover memorandum
TDF
Draft Report (from LIMS)

Data Package Cover [First numbered page in the data package]

Review Forms
- EPA Review Form
- ESAT technical review guide
- *Discrepancy Reports (if applicable)*
- *Work Order Memo (if applicable)*
- Daily folder review forms or checklists
- *Analysis matrix listing all analytical runs (for organics only)*

Tracking Forms
- Work Order(s)
- COC(s)

*Sample Preparation (for projects that require extraction or digestion)*
- Bench Sheets (and copies of notebooks, where used)
- Sample cleanup data and records (e.g. GPC logs)
- Sample homogenization records (for solid/waste/tissue samples)
- Moisture data (when applicable)

[Analysis Method] Data (For each method where multiple methods in package)
- Bench sheet(s) where not used in Sample Preparation section
- Sequence logs and instrument or other data as applicable, in run order and grouped by day.

Alternatively, separate calibration and sample data as:
- Initial Calibration Data (sorted by instrument and then by date)
- Sample Data (sorted by instrument and then by date)

*Miscellaneous Data*
- Other data as applicable (e.g. conductivity for perchlorate)
- Canister certifications (for volatiles in air analysis)

Standard Records
- Standards records from LIMS (and certificates of analysis, if required)

# APPENDIX H.
# REVISION HISTORY

## STANDARD OPERATING PROCEDURE: 530
**Revision: 9, Effective: 06/14/2013**

## ANALYSIS OF ANIONS BY ION CHROMATOGRAPHY

| Revision | Effective Date | Description |
|---|---|---|
| 8 | 10/28/11 | 1. Removed all references to DX-120 and added ICS1100.<br>2. Updated format to current EPA Region 9 Laboratory requirements.<br>3. Updated procedure to follow current internal COC practices.<br>4. Removed reference to instrument runlog. |
| 9 | 06/14/13 | 1. Allowed CCV and LCS requirements to be met with one analysis.<br>2. Added filtered MB requirement when a sample in the batch is filtered.<br>3. Changed calibration range, MS/MSD spike and SCV concentrations of fluoride and bromide.<br>4. Updated matrix QC frequency.<br>5. Minor edits throughout for clarity. |
| | | |
| | | |